USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN STUDY
"The 104 Mill Study"

SUMMARY REPORT

July 1990

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Water Regulations and Standards
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Washington, D.C. 20460

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A. Introduction

In October of 1987 the U.S. Environmental Protection Agency (EPA) and the U.S. pulp and paper industry jointly released preliminary results from a screening study that provided the first comprehensive data on formation and discharge of chlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs) from pulp and paper mills (1). This early screening study of five bleached kraft mills ("Five Mill Study") confirmed that the pulp bleaching process was primarily responsible for the formation of the CDDs and CDFs. The study results showed that 2378-TCDD was present in seven of nine bleached pulps, five of five wastewater treatment sludges, and three of five treated wastewater effluents. The study results also indicated that 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2378-TCDF) were the principal CDDs and CDFs formed. The partitioning of these compounds between the bleached pulp, wastewater treatment sludge, and final wastewater effluent was found to be highly variable among the five mills. The final Five Mill Study report was published in March 1988 (2).

To provide the EPA with more complete data on the release of these compounds by the U.S. industry, an agreement was reached in April 1988 between EPA and the industry to conduct a second study to characterize the 104 U.S. mills that practice chlorine bleaching of chemically produced pulps (3). The scope of the study was developed by EPA and industry, and the study was managed by the National Council of the Paper Industry for Air and Stream Improvement, Inc., (NCASI), with EPA overview. The data from this study provide an estimate of the release of 2378-TCDD and 2378-TCDF in three environmental export vectors (bleached pulp, wastewater sludge, and wastewater effluent) from the U.S. pulp and paper industry as of mid to late 1988.

This summary report presents the major features of the study design, sample collection, and analytical methodologies; a profile of the industry at the time the study was conducted in terms of number and types of mills, number and types of bleach lines, bleach line operating characteristics during sampling, and wastewater treatment; and the study results. This report and a statistical analysis of the data from the study were prepared independently by USEPA (4). The paper industry, through NCASI, has also prepared a report of the 104 Mill Study (5). Preliminary study results were presented by NCASI and EPA in September 1989 (6), and will be published in Chemosphere. This report includes analytical data received by EPA from NCASI as of April 1990. These data comprise virtually all of the analytical data required by the study objectives.

When reviewing the study results, it is important to keep in mind the principal objective of the 104 Mill Study was to

characterize exports from the 104 mills in terms of 2378-TCDD and 2378-TCDF. The study was not designed to address mechanisms of formation of these compounds or to determine what are the best technologies for minimizing formation or treating these compounds in wastewaters. Nonetheless, the study results permit some useful observations in these areas.

The terms used in this report to describe CDDs and CDFs, and pulping, bleaching and wastewater treatment in the pulp and paper industry are defined in the glossary for the Five Mill Study (2).

B. Principal Findings and Conclusions

Industry Profile

1. At the time the 104 Mill Study field program was underway (mid to late 1988 for most mills), the U.S. pulp and paper industry was characterized by only limited application of those pulping and bleaching technologies and operating practices that have been demonstrated to have the potential to reduce formation of 2378-TCDD/TCDF. Since that time, many mill operators have been implementing programs designed to improve pulping and bleaching technologies and operating practices.

Data Summary

2. Analyses of field and laboratory duplicate samples indicated excellent agreement. Consequently, the proportion of total variability in 2378-TCDD/TCDF concentrations which could be attributed to variability in field sampling, or sample handling and analytical techniques, was in all cases small relative to other sources of variability, which are generally attributed to the process.

3. The analytical techniques used are suitable for low-level determinations of 2378-TCDD and 2378-TCDF in kraft mill effluents (i.e., at or below 0.010 ng/kg, or 10 ppq); and, for determinations of 2378-TCDD and 2378-TCDF in bleached pulps and wastewater sludges in the range of 1 ng/kg (or 1 ppt). Target analytical detection levels were achieved or exceeded for most samples and valid data were obtained for nearly all samples.

4. 2378-TCDD and 2378-TCDF were detected in samples from bleached kraft and bleached sulfite mills as follows:

	Kraft Mills	Sulfite Mills
2378-TCDD	90 %	56 %
2378-TCDF	97 %	85 %

No mill was found to be free of 2378-TCDD/TCDF.

5. Detected concentrations of 2378-TCDD and 2378-TCDF were best approximated by lognormal distributions for each of the export vectors: bleached pulp, wastewater sludge and wastewater effluent.

6. The data on concentrations of 2378-TCDD and 2378-TCDF found in the export matrices are summarized below. The number of samples with non-detect analyses (ND's) are listed for each matrix. The mean, median, 90th percentile and maximum values are based upon samples with detected concentrations of 2378-TCDD or 2378-TCDF. Non-detect results were not included in the statistics.

	Number of Samples		(results in ng/kg, or ppt)			
	Detects	ND's	Mean	Median	90%	Maximum
Bleached Pulps						
Kraft Hardwood						
2378-TCDD	62	12	7.5	4.0	17	56
2378-TCDF	72	2	56	17	107	661
Kraft Softwood						
2378-TCDD	98	6	12	7.6	27	116
2378-TCDF	99	3	118	26	185	2620
Sulfite Hardwood						
2378-TCDD	3	5	7.1	4.4	15	15
2378-TCDF	5	3	73	9.9	323	323
Sulfite Softwood						
2378-TCDD	1	7	3.5	3.5	3.5	3.5
2378-TCDF	7	2	125	6.3	449	449
Wastewater Effluents						
Kraft Mills						
2378-TCDD	90	17	0.076	0.035	0.19	0.64
2378-TCDF	104	7	0.48	0.10	1.1	8.4
Sulfite Mills						
2378-TCDD	12	13	0.013	0.012	0.023	0.023
2378-TCDF	21	4	0.11	0.035	0.38	0.84
Wastewater Sludges						
Kraft Mills						
2378-TCDD	94	3	101	39	203	1390
2378-TCDF	97	0	796	161	1728	17100
Sulfite Mills						
2378-TCDD	18	1	13	4.7	48	58
2378-TCDF	16	0	99	63	350	584

Partitioning of 2378-TCDD/TCDF

7. The partitioning of 2378-TCDD and 2378-TCDF to export vectors within mills was found to be highly consistent at most kraft mills.

8. The partitioning of 2378-TCDD and 2378-TCDF to export vectors was highly variable between mills. For all kraft mills, about 38 % of the 2378-TCDD was partitioned to pulps, 33 % to wastewater sludges and 29 % to wastewater effluents.

9. The estimated annualized mass output rates of 2378-TCDD and 2378-TCDF for the kraft and sulfite segment of the U.S. industry at the time of the study were estimated at 1.46 lbs (0.66 kg) and 11.7 lbs (5.31 kg), respectively.

Bleach Plant Practice and Formation of 2378-TCDD/TCDF

10. The formation rates of 2378-TCDD and 2378-TCDF are likely to be somewhat higher than the output rates cited above since the amounts of these compounds that may be partitioned to settled sludges in aerated stabilization basins was not quantified in the sampling program.

11. Correlations between mass export rates of 2378-TCDD/TCDF and a series of kraft mill operating parameters were generally poor. However, positive trends were observed between average formation of 2378-TCDD/TCDF and application of chlorine in the C-Stage and with chlorine multiple (Kappa factor). Increased application of chlorine generally resulted in increased formation of 2378-TCDD/TCDF. Increased substitution of chlorine dioxide generally resulted in decreased formation of 2378-TCDD/TCDF.

Wastewater Treatment

12. On average, mills with activated sludge wastewater treatment systems exported less 2378-TCDD/TCDF to wastewater effluents and more to wastewater sludges than mills with aerated stabilization basin treatment.

13. Correlations between Total Suspended Solids concentrations and 2378-TCDD/TCDF mass outputs for kraft mills were weak, suggesting that TSS levels were at best only partially predictive of 2378-TCDD/TCDF levels in wastewater effluent and wastewater sludge.

2378-Substituted CDDs and CDFs

14. In addition to 2378-TCDD and 2378-TCDF, the most frequently occurring 2378-substituted CDDs and CDFs found in mill exports from nine of the 104 mills included 1234678-HpCDD, OCDD, 12378- and 23478-PeCDF and OCDF.

15. When considered in terms of both the EPA and the I-TEF toxic equivalency approaches, 2378-TCDD and 2378-TCDF account for the vast majority of the computed 2378-TCDD equivalent toxicity in each mill export. Accordingly, current U.S. regulatory programs that are focused on these compounds appear to be properly directed.

C. Study Features

1. Mills included in the 104 Mill Study

All U.S. pulp and paper mills where chemically produced wood pulps are bleached with chlorine and chlorine derivatives were included in the Agreement for the 104 Mill Study (3). However, six bleached kraft mills were not sampled as part of the study. These included the five mills sampled for the Five Mill Study and the Consolidated Papers mill located at Wisconsin Rapids, Wisconsin. Consolidated Papers had independently conducted a study at the Wisconsin Rapids mill. Although mills included in the Five Mill Study were not resampled in the 104 Mill Study, 2378-TCDD/TCDF data and mill operating and wastewater treatment information from the Five Mill Study have been included in this analysis. Due to differences in sampling and analytical protocols, the Consolidated Papers data for 2378-TCDD/TCDF were not included. However, mill operating and wastewater treatment information for Consolidated Papers were included in the industry profiles presented in Section D.

2. Field Sampling Program

The Agreement required that each significant export vector (fully bleached pulp, wastewater sludge, final wastewater effluent) be sampled and the samples composited over a five day period (3). In most cases the composite samples were comprised of up to eight aliquots obtained throughout the sampling day. Nearly all sampling was performed by mill personnel following guidance established by NCASI. In a few cases, NCASI personnel conducted the sampling. The sampling protocols closely followed those established for the Five Mill Study (2).

The pulp samples taken were representative of the highest brightness pulp produced at each bleach line. Hence, at a mill with two bleach lines, where hardwood and softwood pulps are bleached separately, separate hardwood and softwood composite pulp samples were collected. At a mill with a single bleach line where both hardwood and softwood pulps are bleached (i.e., a swing line), sampling was conducted intermittently to ensure the five day composite samples were composed of only hardwood or softwood pulp. At a limited number of mills hardwood/softwood brownstock pulp mixtures are bleached. Bleached pulp from those lines were sampled as noted above for single bleach lines.

Sludge samples consisted of only those sludges removed from the wastewater treatment system and disposed of in landfills, by incineration, or by other methods. Thus, for mills with activated sludge wastewater treatment systems, the sludges sampled generally consisted of combined primary and secondary sludge; for mills with aerated stabilization basins, only primary sludges were sampled. Although in most cases the sludges sampled were dewatered prior to offsite disposal, several primary sludges were collected in a low consistency slurry form.

More than 90 effluents sampled were collected from mills with biological treatment. For eight mills, the samples consisted of partially treated effluents prior to discharge to municipal wastewater treatment plants. Untreated effluents from two mills with direct ocean discharges were sampled. An untreated effluent from a mill with a percolation pond for wastewater disposal was also sampled.

This sampling scheme generated over 400 samples for isomer-specific 2378-TCDD and 2378-TCDF analyses. About 80 additional samples were collected as part of the quality assurance/quality control plan. These samples were analyzed as field duplicates and/or included in native spike determinations. Samples of each export vector from 9 mills were analyzed for all 2378-substituted CDDs and CDFs. The nine mills were chosen by NCASI to represent a variety of bleaching and wastewater treatment configurations.

In addition to the physical samples, mill operators were required to provide process operating data for bleacheries and wastewater treatment plants. These data were collected to document operation of the processes at the time of sampling.

3. Analytical Program

The Brehm Laboratory at Wright State University (WSU), Dayton, Ohio, performed analytical methods development work for isomer-specific determinations of 2378-TCDD and 2378-TCDF in pulp and paper mill matrices, and completed analyses of all samples for the Five Mill Study (2). Analytical work for this study was conducted by Enseco-California Analytical Laboratories (CAL) in West Sacramento, California, and WSU. Enseco-CAL analyzed most of the sludge and effluent samples, while WSU analyzed most of the pulp samples.

The analytical methods used in the 104 Mill Study were consistent with the screening study protocols established for the "Five Mill Study" (2). Analytical objectives for target detection limits for 2378-TCDD and 2378-TCDF were 1 ng/kg(ppt) for sludges and pulps, and 0.01 ng/kg(ppt) for wastewater effluents. The Agreement specified identification and quantitation criteria for 2378-TCDD/TCDF and required that NCASI manage quality

assurance/quality control programs for the study. NCASI staff performed and coordinated sample preparation, submitting samples to the analytical laboratories, and reviewing laboratory data reports. Nearly all analytical results met the quality assurance/quality control objectives established for the study. Less than six percent of the samples required more than one analysis to obtain valid data. This was judged by EPA to be a reasonably small proportion given the study objectives for minimum detection levels and the complexity of the analyses in terms of sample extraction and analyte recovery, identification and quantitation.

4. Data Handling

To ensure consistent reporting of bleach plant and wastewater treatment information, NCASI developed specific forms for use by mill personnel to report bleach line operating characteristics, bleach line chemical applications and wastewater treatment operations. Copies of these forms, as well as schematic diagrams of the bleacheries and wastewater treatment facilities, were provided to EPA by NCASI for most mills. For those few mills for which confidential treatment of certain data were requested, the forms were submitted directly to EPA by mill operators. NCASI submitted final analytical results to EPA as they were developed, in conformance with the quality assurance/quality control protocols specified in the Agreement.

EPA and NCASI independently developed data summaries in spreadsheet format to characterize bleach line operating characteristics; mass flow rates of bleached pulp, wastewater sludge and wastewater effluent; and, mass flows of 2378-TCDD and 2378-TCDF in the mill exports. The respective spreadsheet entries were compared several times and corrections were made as appropriate. Prior to conducting detailed statistical analyses, EPA had a contractor further compare the EPA spreadsheets against the original report forms. All discrepancies were resolved and the spreadsheets were updated accordingly. New databases were then created by uploading the data from the spreadsheets to the EPA mainframe computer.

As data were received from NCASI, the Industrial Technology Division compiled summaries of bleached pulp, wastewater sludge and wastewater effluent concentrations and distributed the results to EPA regional offices and state agencies. On May 4, 1989, EPA determined that certain bleach plant process data supplied by mill operators should be provided confidential treatment, but that bleached pulp data for 2378-TCDD/TCDF and other miscellaneous bleach plant data were not confidential. The data summaries presented in this report do not disclose confidential bleach plant data.

D. Industry Profile

1. Pulping and Bleaching

Tables 1 and 2 present the profiles for pulping and bleaching, respectively, for those mills included in the study. This segment of the U.S. industry is comprised of 86 kraft pulping mills, 16 sulfite mills, one soda mill and one mill with both kraft and sulfite pulping. More than half of the bleach lines at kraft mills are used for bleaching softwoods exclusively and forty percent for bleaching hardwoods. The balance are either swing lines or are used to bleach hardwood/softwood pulp mixtures. For sulfite mills, half the bleach lines are used for bleaching softwood pulps, nearly 40% for hardwood pulps and the balance for mixed pulps.

Table 1: Industry Profile - Pulping

	Number of Mills
Kraft	86
Sulfite	16
Kraft and Sulfite	1
Soda	1
Total	104

Table 2: Industry Profile - Bleaching

	Number of Bleach Lines		
	Kraft	Sulfite	Soda
Hardwood	67	7	1
Softwood	89	9	-
Mixed HW/SW	9	2	-
Total	165	18	1

Note: (1) Kraft hardwood and softwood bleach line data include 14 swing lines. Each swing line was counted as both a hardwood and a softwood line, where appropriate; or, as two hardwood or softwood lines where multiple grades of the same species were bleached.

2. Bleach Line Chemical Usage

Table 3 presents a summary of the number and percentage of bleach lines with oxygen delignification systems and chemical use in pre-bleaching and final bleaching. The data were provided by mill operators to characterize operations during the sampling surveys.

Table 3: Industry Profile - Bleach Line Chemical Usage

	Number of Bleach Lines, (%)	
	Kraft and Soda	Sulfite
Oxygen Delignification	7 (4.2)	1 (5.6)
Pre-bleaching		
Chlorine Stage Cl2	166 (100)	16 (89)
Chlorine Stage ClO2	106 (64)	1 (5.6)
Extraction Stage O2	79 (48)	4 (22)
Extraction Stage NaOCl	47 (28)	1 (5.6)
Extraction Stage H2O2	2 (1.2)	1 (5.6)
Final Bleaching		
ClO2	148 (89)	4 (22)
NaOCl	90 (54)	14 (78)
H2O2	25 (15)	1 (5.6)

As shown above, the industry was characterized by low utilization of oxygen delignification, relatively low utilization of oxygen reinforced extraction, low utilization of peroxide reinforced extraction, and relatively high utilization of hypochlorite in both pre-bleaching and final bleaching.

The status of bleachery operations of the U.S. industry in mid to late 1988 with respect to chlorine usage and chlorine dioxide substitution is summarized in Table 4. Note that about 35 % of the kraft mill bleach lines were operated with no chlorine dioxide in the Chlorine Stage (C-Stage), and less than 2 % had chlorine dioxide substitution rates greater than 50 %, a level which has been demonstrated to have significant positive effects for minimizing formation of several chlorinated organic compounds, and 2378-TCDD/TCDF in particular (7).

Table 4: Status of U.S. Bleachery Operations C-Stage Chlorination and Chlorine Dioxide Substitution (1988)

Chlorine Application lbs Cl2/ton ADBSP	Bleach Lines	ClO2 Substitution percent	Bleach Lines
Kraft Mill Bleach Lines			
< 40 lbs/ton	15	0 %	59
40-60	22	< 5	16
60-80	32	5 - 10	41
80-100	36	10 - 20	33
100-120	28	20 - 30	9
120-140	16	30 - 40	1
> 140	16	40 - 50	3
		50 - 60	1
TOTAL	165	60 - 70	1
		> 70	1
		TOTAL	165
Sulfite Mill Bleach Lines			
< 40 lbs/ton	2	0 %	17
40-60	1	< 5	1
60-80	2	> 5	0
80-100	6		
100-120	3	TOTAL	18
120-140	4		
> 140	0		
TOTAL	18		

Notes: (1) Bleachery operations for swing lines were counted separately for hardwood and softwood pulps.
(2) ADBSP - Air-dried brownstock pulp.

Table 5 presents a summary of 5 day average chlorine multiples (Kappa factor) determined for kraft and sulfite bleach lines at the time of sampling. The chlorine multiple is the ratio of the amount of active chlorine used in pulp bleaching in the C-Stage, to the amount of lignin contained in brownstock or oxygen delignified pulp as characterized by the Kappa number. At the time of the mill sampling programs, 11 per cent of bleach lines were operated with average chlorine multiples less than 0.15, a level which has been cited as a threshold below which formation of 2378-TCDD/TCDF is greatly reduced (7). The average chlorine multiple over an extended period may not be a good measure of the 2378-TCDD/TCDF-forming potential of a pre-bleaching operation since short term variations above 0.15 are thought to be significant.

Table 5: C-Stage Chlorine Multiple (Kappa Factor)

Chlorine Multiple	Number of Bleach Lines Kraft	Sulfite
< 0.10	4	2
0.10 - < 0.15	15	1
0.15 - < 0.20	51	6
0.20 - < 0.25	54	3
0.25 - < 0.30	17	-
> 0.30	14	6
Total	155	18

Notes: (1) Chlorine multiple was computed from active chlorine (Cl2 and ClO2) applied in the C-Stage.
(2) Chlorine multiples could not be computed for ten kraft mill bleach lines because of incomplete data.

On balance, pulping and bleaching facilities were not operated to minimize formation of 2378-TCDD/TCDF at the time of the 104 Mill Study. Presently, there are several bleachery upgrades underway, many of which include partial extended delignification, increasing capability for chlorine dioxide substitution, modification of caustic extraction systems and installation of oxygen delignification systems.

3. Wastewater Treatment

The status of wastewater treatment provided at the 104 mills is summarized in Table 6. The industry standard is primary treatment followed by secondary biological treatment. Eight mills discharge to POTWs after primary treatment and two have no treatment. Wastewaters from one mill are disposed of in a percolation pond. For the kraft segment, about 35 % of the mills have activated sludge treatment and more than half have aerated stabilization basins. For sulfite mills, nearly 70 % have activated sludge systems and nearly 20 % have aerated stabilization basins.

Table 6: Industry Profile - Wastewater Treatment

	Number of Mills			
	Kraft	Sulfite	Soda	Total
Activated Sludge	32	11	-	43
Aerated Stabilization Basin	45	3	1	49
Discharge to POTW	7	1	-	8
Discharge to Other Mill WWTP	-	1	-	1
Percolation Pond	1	-	-	1
No Treatment	2	-	-	2
Total	87	16	1	104

Note: (1) The mill with kraft and sulfite pulping was listed as a kraft mill for purposes of this table.

E. Summary of Results

Examination of analytical data from samples collected at each mill indicated detected concentrations of 2378-TCDD/TCDF were best approximated by lognormal distributions, estimated separately for each of the export matrices: bleached pulp, sludge, and effluent.

Estimates of non-detected measurements were required for the analyses of results. For the purposes of this study, these measurements were assigned a value equal to half the detection limit. This compromise procedure has been used in other studies and enables information from non-detect samples to be utilized (4). This procedure was judged reasonable in light of the significant proportion of all samples with detectable concentrations of 2378-TCDD/TCDF, and the consistent partitioning of 2378-TCDD and 2378-TCDF within mills. In this study, and in the Five Mill Study, no mill was found to be free of 2378-TCDD/TCDF.

About 30% of all the samples analyzed were field duplicate samples or laboratory-split duplicate samples. Analysis of these duplicate samples indicated that within each matrix (pulp, sludge and effluent), excellent agreement was shown between repeated measurements of 2378-TCDD/TCDF concentration. Most correlations between pairs of duplicate measurements were found to be greater than 0.95. Consequently, the proportion of total variability in 2378-TCDD/TCDF levels which could be attributed to variability in field sampling protocol or analytical technique was in all cases small relative to other sources of variability, which are generally attributed to the pulping and bleaching processes. This finding

supports averaging of duplicate pair results for purposes of estimating mass flow rates of 2378-TCDD/TCDF, as was done in this study.

The analytical techniques used are suitable for low-level determinations (i.e., in the range of and below 0.010 ng/kg, (10 ppq)), of 2378-TCDD/TCDF in kraft mill wastewater effluents. Analysis of sulfite mill effluents may not be as precise over a larger range. The study results also indicate the analytical methods are suitable for determinations of 2378-TCDD/TCDF in the range of 1 ng/kg (1 ppt) for bleached pulps and wastewater sludges.

1. Bleached Pulps

Summary statistics of 2378-TCDD/TCDF concentrations expressed as ng/kg(ppt) in the bleached pulps are presented in Table 7. The data are reported by pulping type (kraft and sulfite) as well as by wood specie (hardwood and softwood). The statistics include number of samples with non-detect results, number of samples with detectable results, and mean, median, 90th percentile and maximum concentrations. Non-detect analytical results were not included for calculation of mean, median and 90th percentile concentrations.

Table 7: 2378-TCDD/TCDF Concentrations in Bleached Pulps

	Number of Samples		Mean	Median	90 %	Maximum
	ND	Detect	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
HW Kraft Pulps						
2378-TCDD	12	62	7.5	4.0	17	56
2378-TCDF	2	72	56	17	107	661
SW Kraft Pulps						
2378-TCDD	6	98	12	7.6	27	116
2378-TCDF	3	99	118	26	185	2620
HW Sulfite Pulps						
2378-TCDD	5	3	7.1	4.4	15	15
2378-TCDF	3	5	73	9.9	323	323
SW Sulfite Pulps						
2378-TCDD	7	1	3.5	3.5	3.5	3.5
2378-TCDF	2	7	125	6.3	449	449

Note that these findings are representative of the 104 mills as of mid to late 1988 when most of the sampling was completed.

Since that time several mill operators have been implementing process changes designed to reduce 2378-TCDD/TCDF concentrations in bleached pulps. Although the net effect of these changes on formation of 2378-TCDD/TCDF is not fully known or quantified at this time, examination of preliminary results supplied by mill operators indicate significant reductions in formation of 2378-TCDD/TCDF may be possible.

Correlating the above pulp findings with pulping or bleach plant process parameters was significantly limited because 2378-TCDD/TCDF concentrations in bleached pulp represent only a portion of that formed in the bleach plant. The "Five Mill Study" clearly demonstrated that bleach plant filtrates represented a significant fraction of the total mass of 2378-TCDD/TCDF formed, and the distribution between the pulp and filtrate phases was highly variable from mill to mill (1,2). That finding was confirmed by the more extensive data obtained from this study, (see Section D.3). Hence, correlations of bleach plant operations with only pulp data would not be valid and are not presented. Because it was not the objective of this study to fully investigate the impact of pulping and bleaching process parameters on 2378-TCDD/TCDF formation in the bleach plant, filtrate samples were not collected.

2. Wastewater Effluents and Wastewater Sludges

Tables 8 and 9 present summary statistics of 2378-TCDD/TCDF concentrations in wastewater effluents and sludges, respectively. The summary statistics are the same as those presented for bleached pulps in Table 7. Data for kraft mills and sulfite mills are distinguished. Samples of wastewater sludge slurries obtained at a number of mills (generally less than 5% solids) were analyzed as liquids. Although these data were not included in Table 9, they were considered in mass flow calculations for the respective mills.

Table 8: 2378-TCDD/TCDF Concentrations in Wastewater Effluents

	Number of Samples		Mean	Median	90 %	Maximum
	ND	Detect	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
Kraft Mills						
2378-TCDD	17	90	0.076	0.035	0.19	0.64
2378-TCDF	7	104	0.48	0.10	1.1	8.4
Sulfite Mills						
2378-TCDD	13	12	0.013	0.012	0.023	0.023
2378-TCDF	4	21	0.11	0.035	0.38	0.84

Note: (1) A few mills have more than one wastewater effluent. All available effluent data are included.

Table 9: 2378-TCDD/TCDF Concentrations in Wastewater Sludges

	Number of Samples ND	Detect	Mean (ng/kg)	Median (ng/kg)	90 % (ng/kg)	Maximum (ng/kg)
Kraft Mills						
2378-TCDD	3	94	101	39	203	1,390
2378-TCDF	0	97	796	161	1728	17,100
Sulfite Mills						
2378-TCDD	1	18	13	4.7	48	58
2378-TCDF	0	16	99	63	350	584

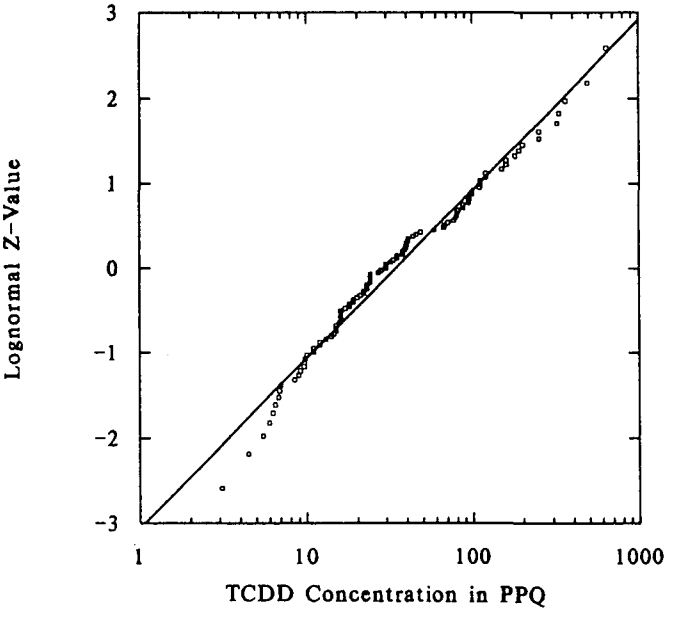
Note: (1) Analytical results for dewatered sludges are included; results for sludge slurries are not included.

The effluent and sludge concentrations measured for sulfite mills were generally less than those for kraft mills, as was the case for bleached pulps described in Table 7. In all exports, the concentrations of 2378-TCDD/TCDF were found to be highly variable and distributed lognormally. Figure 1 presents the distribution of 2378-TCDD in wastewater effluents. Distributions of 2378-TCDD and 2378-TCDF were similar for all exports.

Figure 1

EFFLUENT TCDD

PROBABILITY PLOT: DETECTED VALUES ONLY



3. Mass Flows of 2378-TCDD/TCDF

Rates of 2378-TCDD/TCDF mass flow were computed for all matrices at each mill by combining the 2378-TCDD/TCDF concentration data with mill production rates of pulp, sludge and effluent. Estimates of mass output rates of 2378-TCDD and 2378-TCDF at U.S. bleached pulp mills were 1.46 lbs/yr (0.66 kg/yr) and 11.7 lbs/yr (5.31 kg/yr), respectively. Output rates varied substantially from mill to mill. Comparisons showed that significantly more 2378-TCDD/TCDF was exported at kraft mills than at sulfite mills.

The summary statistics of total mill exports of 2378-TCDD/TCDF from kraft and sulfite mills are highlighted in Table 10. These results are presented in terms of lbs/ton of air-dried brownstock pulp (ADBSP) and include data from only those mills with complete mass flow data for pulp, sludge, and effluent and complete analytical data for 2378-TCDD/TCDF.

Note that calculated total mill mass flow rates for mills with aerated stabilization basins may not fully reflect the rates of formation of 2378-TCDD/TCDF. The results for those mills are probably biased low due to retention of 2378-TCDD/TCDF in sludge in aerated lagoons which would not have been characterized by the sampling program. Accordingly, the results presented are believed to be representative of total mill exports for all mills at the time of sampling, but not necessarily fully representative of the total amount of 2378-TCDD/TCDF formed.

Table 10: Total Mill Exports of 2378-TCDD/TCDF

(Results in 10-8 lbs/ton ADBSP)

	Number of Mills	Mean	Median	90 %	Maximum
Kraft Mills					
2378-TCDD	80	4.9	2.8	12	31
2378-TCDF	80	48	10	123	954
Sulfite Mills					
2378-TCDD	14	1.0	0.46	3.3	4.5
2378-TCDF	14	14	3.5	73	145

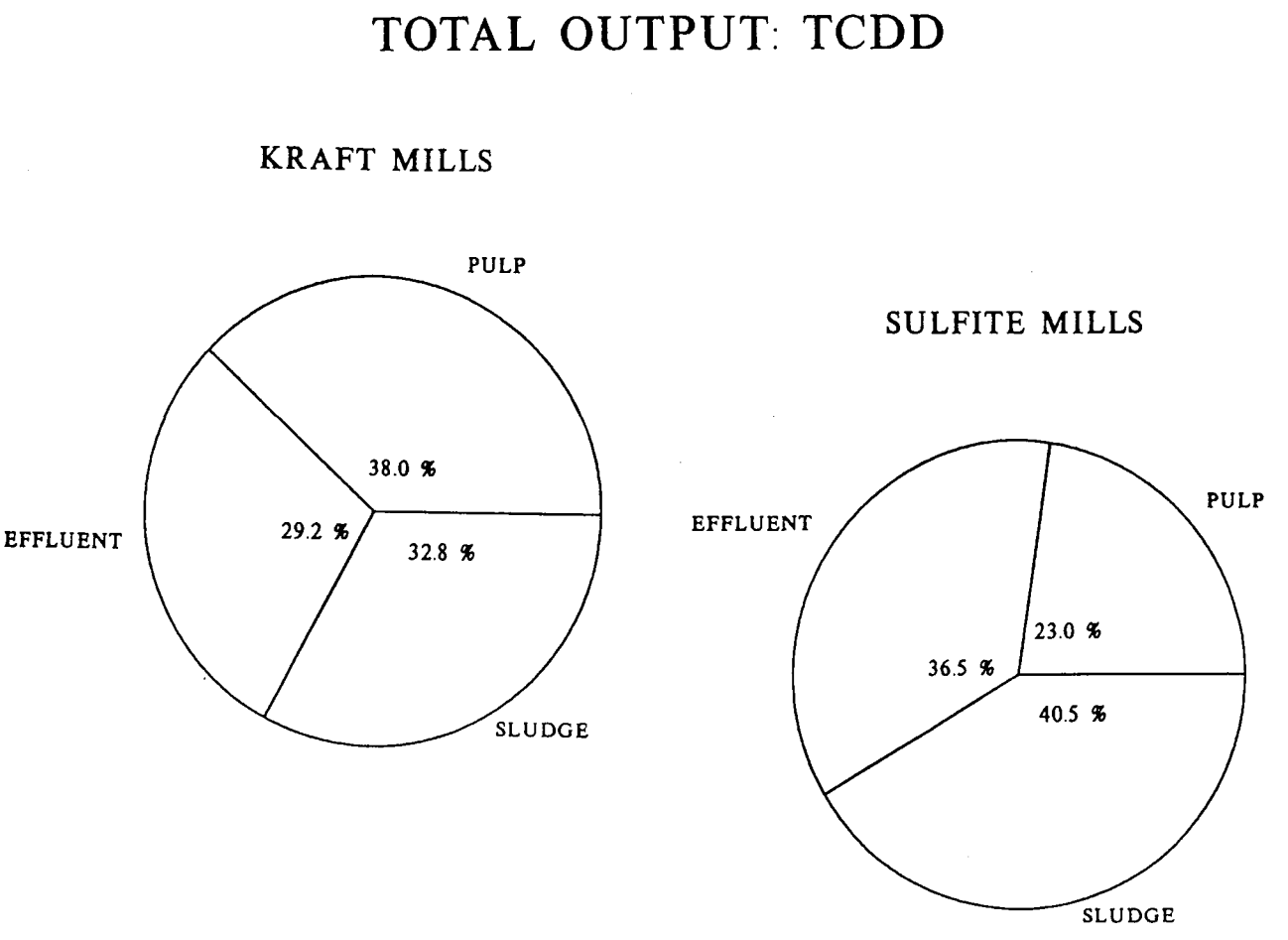
Notes: (1) Only results for mills with complete analytical and mass flow data are included.

(2) Mass flow calculations for several mills are affected by sludge retention in aerated stabilization basins.

(3) ADBSP - Air-Dried Brownstock Pulp

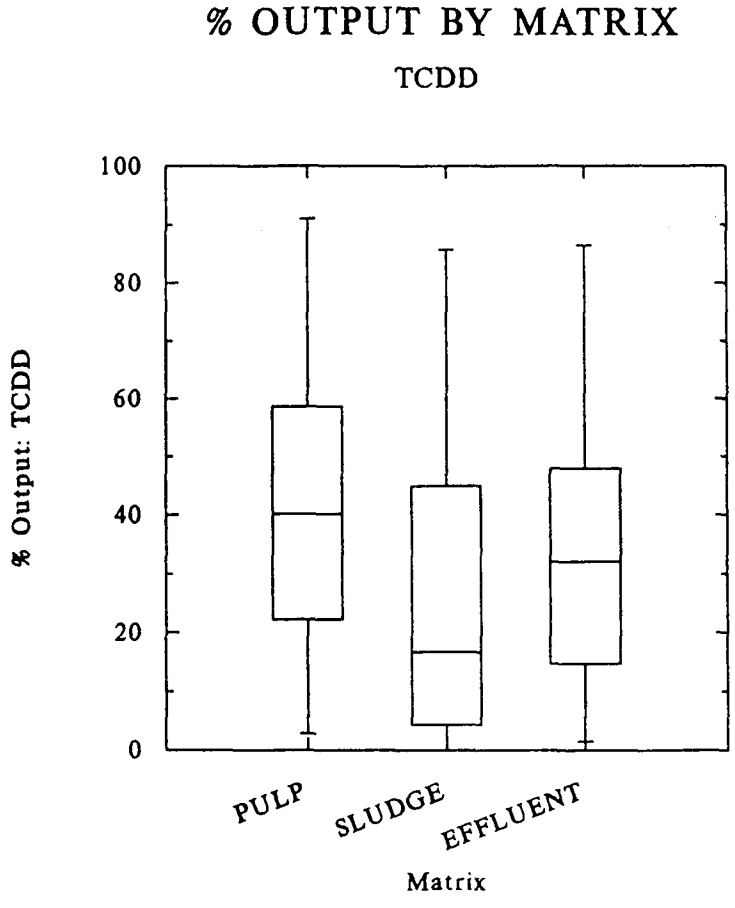
Figure 2 illustrates the distribution of estimated mass flows of 2378-TCDD among pulp, effluent and sludge for kraft and sulfite mills on an industry-wide basis.

Figure 2



The high variability of the partitioning of 2378-TCDD among exports on a mill to mill basis is highlighted in Figure 3. The results for 2378-TCDF were similar. Each boxplot shown in Figure 3 was constructed such that the top and bottom edges of the box represent the upper and lower quartiles of the distribution of percentages taken across all mills. The line dividing each box is the median, and the middle 95% of all data is depicted by the extensions above and below each box.

Figure 3



As was the case with the Five Mill Study results, within-mill partitioning of 2378-TCDD among mill exports compared to that of 2378-TCDF was found to be consistent. Although statistical analyses were not conducted to fully examine this phenomenon, the maximum difference between partitioning of 2378-TCDD and 2378-TCDF among pulp, sludge and effluent at 80 % of kraft mills was found to be less than 20 %.

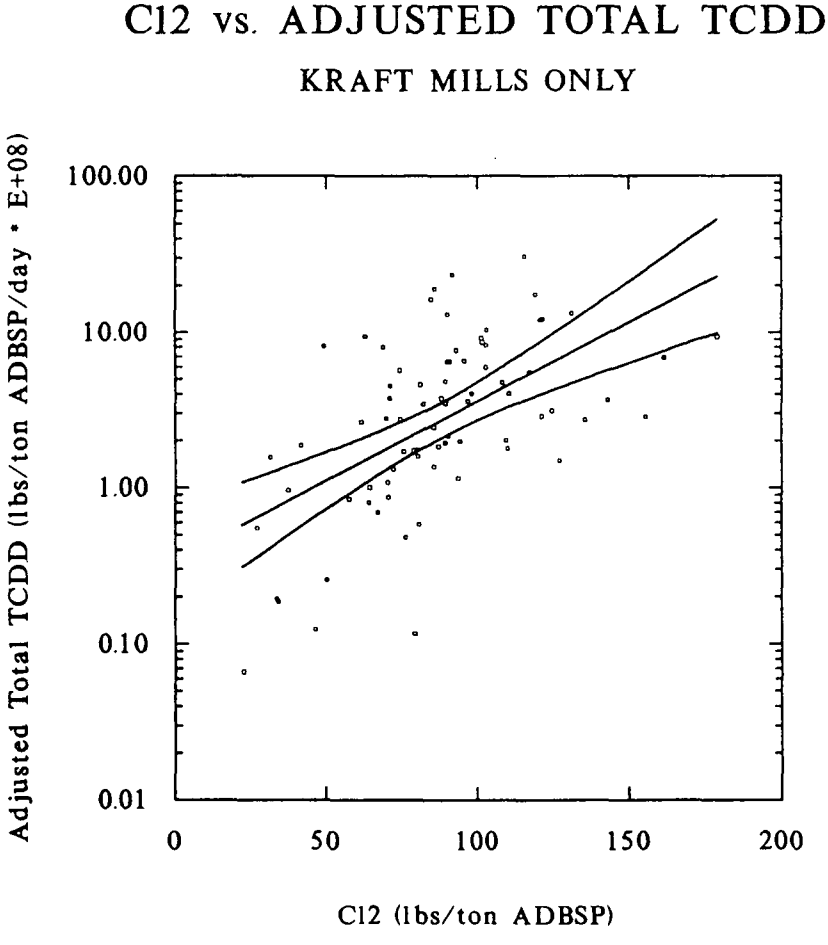
4. Bleaching Practice and Formation of 2378-TCDD/TCDF in Kraft Mills

Analyses were completed on the effects of mill bleaching procedures upon formation of 2378-TCDD/TCDF. Correlations between mass export rates of 2378-TCDD/TCDF and a series of mill parameters (including application rates of bleaching and extraction chemicals) were generally quite low. Consequently, linear regressions of the 2378-TCDD/TCDF export rates fit to each bleaching parameter were found to be poor predictors of individual mill outputs. However,

significant positive trends were observed between average 2378-TCDD/TCDF formation and the rate of application of chlorine in the C-Stage.

Figure 4 is a plot of 2378-TCDD formed, as characterized by export vector measurements, vs chlorine applied in the C-Stage for kraft mills. The data indicate a general trend of increasing 2378-TCDD with increasing chlorine application; although, as noted above, there appears to be only a weak correlation. Plots of 2378-TCDD vs chlorine ratio or kappa factor for all kraft mills yielded similar results. Increased substitution of chlorine dioxide for chlorine in the C-Stage was weakly correlated with decreased formation of 2378-TCDD/TCDF mass.

Figure 4



For certain mills, factors other than chlorine application appear to have had a more significant impact on formation of 2378-TCDF than on formation of 2378-TCDD. This resulted in

uncharacteristically high ratios of 2378-TCDF to 2378-TCDD. In a number of cases use of contaminated oil-based defoamers was reported to be responsible for the unusually high formation of 2378-TCDF. Resampling at a few mills after substitutions were made confirmed this finding.

5. Kraft Mill Wastewater Treatment Findings

Differences emerged between mills with Aerated Stabilization Basin (ASB) and Activated Sludge (ACT) wastewater treatment systems. There was significant evidence that mills using ACT treatment exported less effluent-based 2378-TCDD/TCDF and more sludge-based 2378-TCDD/TCDF on average than mills with ASB systems. This is principally due to differences in management of biological solids in each type of system; and, the method of sludge sampling conducted for this study, which did not characterize sludge stored in ASB systems. Figures 5 and 6 illustrate the above findings for 2378-TCDD. Results for 2378-TCDF were similar.

Figure 5

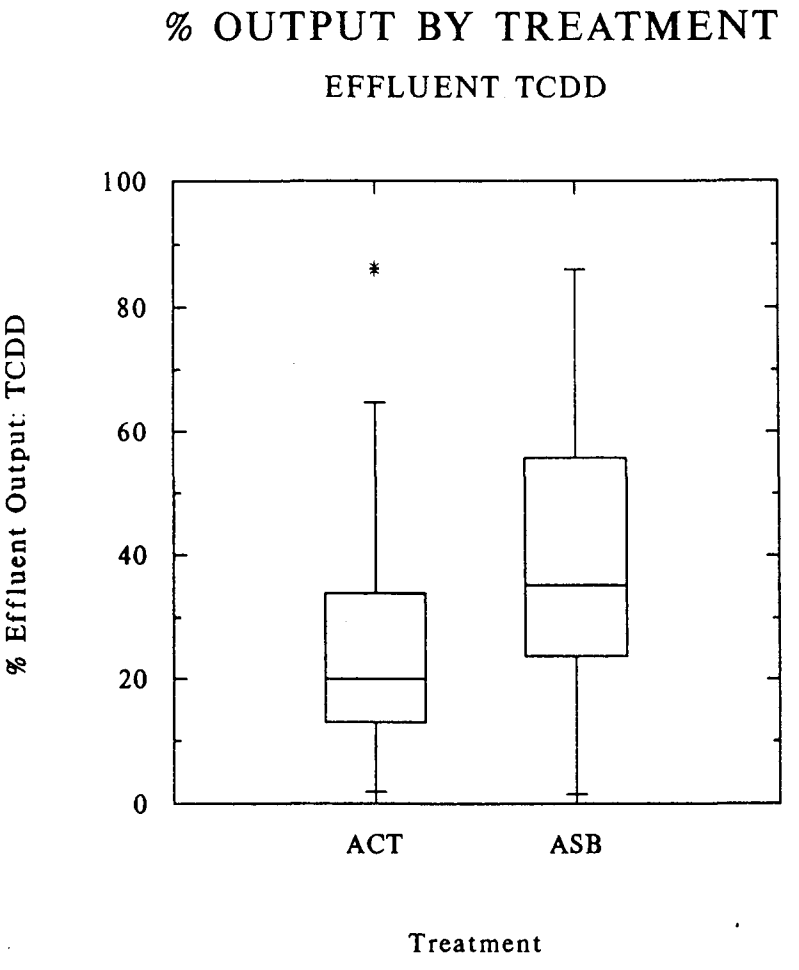
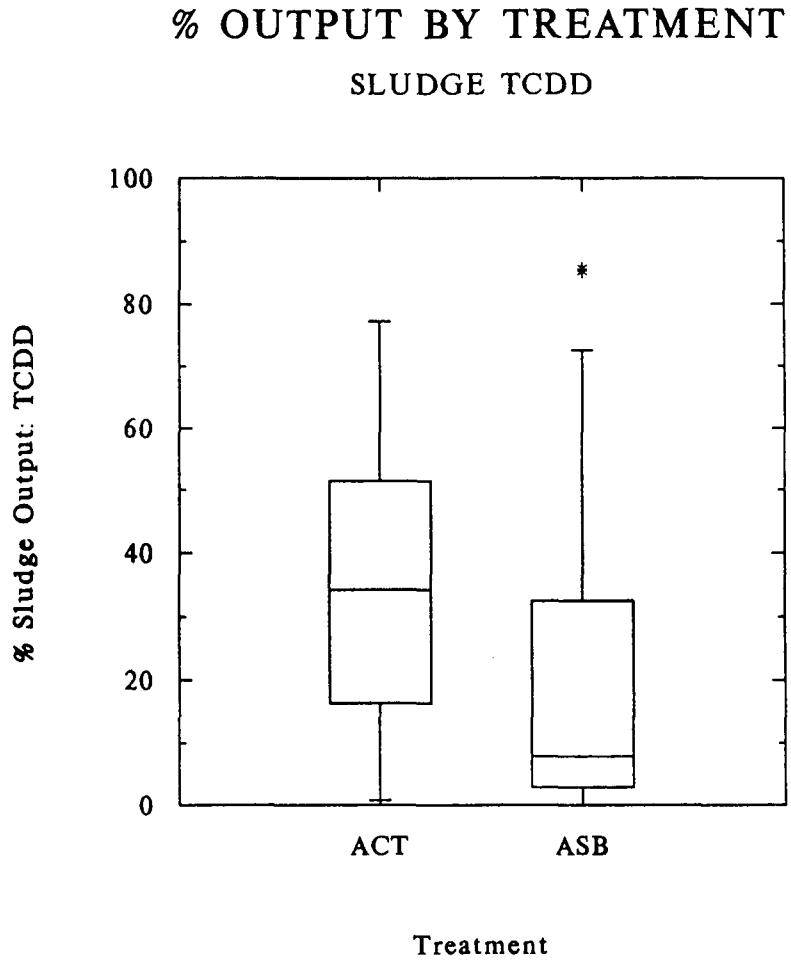


Figure 6



Further investigations were made of possible relationships between 2378-TCDD/TCDF mass exports in sludge and effluent, type of wastewater treatment provided, and levels of Total Suspended Solids (TSS). On average, TSS concentrations in ACT treatment system effluents were found to be higher than those in ASB treatment system effluents, (60 mg/l vs 48 mg/l). Correlations between effluent concentrations of TSS and 2378-TCDD/TCDF mass outputs were fairly weak, suggesting that TSS levels were at best only partially predictive of 2378-TCDD/TCDF partitioning to sludge and effluent.

When data from ACT and ASB-type mills were combined, a significant but weakly correlated positive trend was observed between effluent 2378-TCDD/TCDF mass and TSS concentrations. A weakly correlated negative trend was observed between TSS and sludge 2378-TCDD/TCDF. For kraft mills using ACT treatment, higher TSS levels were associated with higher sludge-based 2378-TCDD/TCDF exports and lower effluent-based 2378-TCDD/TCDF exports

6. Other 2378-Substituted CDDs and CDFs

Bleached pulp, wastewater sludge and final wastewater effluent samples from eight kraft mills and one sulfite mill were analyzed for 2378-substituted CDDs and CDFs, and total CDDs and CDFs by homologue class, tetra through octa. These analyses were conducted to test the conclusion drawn in the Five Mill Study that 2378-TCDD and 2378-TCDF were the principal CDDs and CDFs found in pulp and paper mill exports, when considered in terms of EPA's toxic equivalence approach (8).

The analyses were completed by Enseco-CAL. Ten bleached pulps, 9 wastewater sludges and 9 final wastewater effluents were analyzed. Duplicate analyses were conducted on one sample from each matrix. Although there are no reference analytical methods for many of the 2378-substituted CDDs and CDFs, the data obtained are considered valid for the purposes intended based upon the identification and quantitation criteria used, duplicate sample results and limited matrix spike experiments.

Tables 11, 12 and 13 present summaries of the results obtained in terms of the median concentration and the range of concentrations determined for each matrix, respectively. Examination of the raw data and the data summaries show that the patterns of isomer profiles were fairly consistent across matrices within mills. The most common 2378-substituted CDDs and CDFs found in mill exports, in addition to 2378-TCDD and 2378-TCDF, were 1234678-HpCDD, OCDD, 12378- and 23478-PeCDF, and OCDF. Non-2378-substituted tetra-, penta- and hexa-CDDs and CDFs were often found at greater frequency among the nine mills than the corresponding 2378-substituted compounds.

Tables 14 presents the 2378-TCDD toxic equivalent concentrations (2378-TECs) for the median values presented in Tables 11, 12 and 13, and for the sample from each matrix containing the highest concentrations of CDDs and CDFs. The 2378-TECs were computed using the EPA and the I-TEF toxic equivalency approaches (8). Table 15 presents comparisons of the percentages of the 2378-TECs attributable to 2378-TCDD and 2378-TCDF. These comparisons were made assuming non-detected CDDs and CDFs were present at the detection level, and were not present, (i.e., zero concentration). The results indicate, even with the most conservative assumptions, that 2378-TCDD and 2378-TCDF account for the vast majority of the 2378-TEC in each sample. This finding is consistent with results from the Five Mill Study (2).

Bleached pulps manufactured in British Columbia from sawdust recycled from certain wood treating operations have exhibited markedly different isomer profiles, with the HxCDDs more prevalent. Those findings have been linked to pentachlorophenol-based wood treating operations (9). This phenomena is not expected in the United States since such materials are not suspected of being used as sources of fiber at U.S. pulping or bleaching operations.

Table 11: Pulp and Paper Mill Bleached Pulps
Tetra- through Octa-CDDs and CDFs

(Results in ng/kg, or ppt)

	Median	Range	No. of Detects (10 samples)
2378-TCDD	6.4	0.4 to 124	10
Other TCDDs	ND (0.4)	ND (0.2) to 7.0	2
12378 PeCDD	ND (0.3)	ND (0.1) to 1.4	2
Other PeCDDs	ND (0.3)	ND (0.1) to 2.1	3
123478 HxCDD	ND (0.4)	ND (0.2) to 0.4	1
123678 HxCDD	ND (0.5)	ND (0.2) to 1.6	2
123789 HxCDD	ND (0.5)	ND (0.2) to 0.5	1
Other HxCDD	ND (0.5)	ND (0.2) to 8.8	3
1234678 HpCDD	3.3	2.3 to 8.4	10
Other HpCDDs	2.8	1.9 to 8.4	10
OCDD	46	28 to 81	10
2378-TCDF	18	1.4 to 716	10
Other TCDFs	37	2.7 to 810	10
12378 PeCDF	ND (0.7)	ND (0.1) to 3.9	4
23478 PeCDF	ND (0.2)	ND (0.1) to 4.7	3
Other PeCDFs	4.5	ND (0.2) to 17	9
123478 HxCDF	ND (0.3)	ND (0.2) to ND (0.6)	0
123678 HxCDF	ND (0.3)	ND (0.1) to ND (0.4)	0
234678 HxCDF	ND (0.3)	ND (0.2) to ND (0.4)	0
123789 HxCDF	ND (0.3)	ND (0.1) to ND (0.4)	0
Other HxCDFs	ND (0.4)	ND (0.2) to 1.7	4
1234678 HpCDF	ND (0.6)	ND (0.1) to 0.8	3
1234789 HpCDF	ND (0.6)	ND (0.1) to ND (2.1)	0
Other HpCDFs	ND (0.6)	ND (0.1) to 2.3	3
OCDF	2.2	ND (2.8) to 4.3	8

Table 12: Pulp and Paper Mill Wastewater Sludges
Tetra- through Octa-CDDs and CDFs

(Results in ng/kg, or ppt)

	Median	Range	No. of Detects (9 samples)
2378-TCDD	63	ND (6.3) to 180	8
Other TCDDs	ND (1.5)	ND (1.1) to 837	2
12378 PeCDD	ND (2.5)	ND (1.4) to 28	1
Other PeCDDs	ND (2.9)	ND (1.6) to 1,280	2
123478 HxCDD	ND (3.1)	ND (1.5) to 40	1
123678 HxCDD	ND (3.2)	ND (1.7) to 95	1
123789 HxCDD	ND (3.9)	ND (1.7) to 80	1
Other HxCDD	11	ND (3.1) to 2,180	8
1234678 HpCDD	37	18 to 490	9
Other HpCDDs	35	18 to 447	9
OCDD	698	263 to 1,780	9
2378-TCDF	233	13 to 1,150	9
Other TCDFs	547	37 to 2,310	9
12378 PeCDF	6.2	ND (1.2) to 22	6
23478 PeCDF	4.7	ND (0.9) to 38	6
Other PeCDFs	14	ND (2.0) to 268	5
123478 HxCDF	ND (2.5)	ND (0.9) to 31	2
123678 HxCDF	ND (1.4)	ND (0.9) to 33	1
234678 HxCDF	ND (1.7)	ND (0.9) to 34	1
123789 HxCDF	ND (1.7)	ND (0.9) to ND (4.0)	0
Other HxCDFs	5.2	ND (0.9) to 219	7
1234678 HpCDF	6.6	ND (3.6) to 70	7
1234789 HpCDF	ND (1.6)	ND (1.2) to 10	1
Other HpCDFs	12.7	ND (1.2) to 63	8
OCDF	22	ND (54) to 168	8

Table 13: Pulp and Paper Mill Wastewater Effluents
Tetra- through Octa-CDDs and CDFs

(Results in pg/kg, or ppq)

	Median	Range	No. of Detects (9 samples)
2378-TCDD	42	ND (11) to 98	8
Other TCDDs	34	ND (3) to 138	7
12378 PeCDD	ND (9.6)	ND (2.8) to ND(25)	0
Other PeCDDs	9.6	ND (9.6) to 130	5
123478 HxCDD	ND (12)	ND (6.6) to ND (12)	0
123678 HxCDD	ND (12)	ND (6.6) to ND (24)	0
123789 HxCDD	ND (12)	ND (6.6) to ND (23)	0
Other HxCDDs	ND (17)	ND (6.6) to ND 360	4
1234678 HpCDD	170	77 to 270	9
Other HpCDDs	120	ND (27) to 160	8
OCDD	3,000	1,000 to 4,600	9
2378-TCDF	120	12 to 840	9
Other TCDFs	270	43 to 1,460	9
12378 PeCDF	ND (7.2)	ND (2.2) to 36	2
23478 PeCDF	ND (6.3)	ND (2.2) to 33	2
Other PeCDFs	21	ND (2.2) to 71	5
123478 HxCDF	ND (8.4)	ND (4.8) to ND (15)	0
123678 HxCDF	ND (7.1)	ND (4.8) to ND (15)	0
234678 HxCDF	ND (8.2)	ND (4.8) to ND (15)	0
123789 HxCDF	ND (6.2)	ND (2.5) to ND (15)	0
Other HxCDFs	ND (15)	ND (5.2) to 54	4
234678 HpCDF	ND (23)	ND (13) to 44	3
1234789 HpCDF	ND (22)	ND (6.4) to ND (41)	0
Other HpCDFs	36	ND (13) to 79	7
OCDF	190	ND (180) to 230	8

Table 14: 2378-TCDD Toxic Equivalents
Nine Mill Sampling Program

(Results in ng/kg, or ppt)

	EPA-TEF/87		I-TEFs/89	
	ND=0	ND=DL	ND=0	ND=DL
BLEACHED PULP				
Median	8.24	8.56	8.28	8.83
Worst case	197.4	198.2	198.4	199.4
WASTEWATER SLUDGE				
Median	88.0	89.8	90.1	93.1
Worst case	216.3	220.6	218.5	223.8
WASTEWATER EFFLUENT				
Median	0.055	0.063	0.059	0.073
Worst case	0.142	0.156	0.147	0.177

Note: (1) "Worst case" represents the sample with the highest levels of 2378-substituted CDDs and CDFs.

Table 15: 2378-TCDD Toxic Equivalents
Nine Mill Sampling Program
Percent of 2378-TEC Attributable to 2378-TCDD/TCDF

(Results in percent, %)

	EPA-TEF/87		I-TEFs/89	
	ND=0	ND=DL	ND=0	ND=DL
BLEACHED PULP				
Median	99.5	95.8	99.0	92.8
Worst case	99.1	98.7	98.6	98.1
WASTEWATER SLUDGE				
Median	98.1	96.1	95.8	92.7
Worst case	98.4	96.4	97.4	95.1
WASTEWATER EFFLUENT				
Median	98.4	86.0	91.7	72.7
Worst case	98.6	89.7	95.1	79.0

Note: (1) "Worst case" represents the sample with the highest levels of 2378-substituted CDDs and CDFs.

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